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EVIDENCE FOR THE STRUCTURES OF ADSORBED NH<sub>3</sub> AND H<sub>2</sub>O ON RU(001), (U)  
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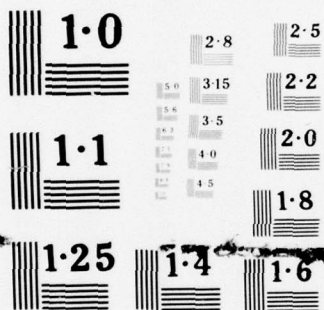
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TECHNICAL REPORT

EVIDENCE FOR THE STRUCTURES OF ADSORBED  $\text{NH}_3$  AND  $\text{H}_2\text{O}$  ON  $\text{Ru}(001)$

by

Theodore E. Madey and John T. Yates, Jr.

Surface Processes and Catalysis Section

National Bureau of Standards

Washington, DC 20234

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National Bureau of Standards, Washington, DC 20234

**Abstract:** The adsorption of  $\text{NH}_3$  and  $\text{H}_2\text{O}$  on  $\text{Ru}(001)$  have been studied using the Electron Stimulated Desorption Ion Angular Distribution (ESDIAD) method, in conjunction with thermal desorption spectroscopy and LEED. The results suggest that chemisorbed  $\text{NH}_3$  and  $\text{H}_2\text{O}$  are bonded to Ru via the N and O atoms, respectively, with H atoms pointed away from the surface. The utility of ESDIAD for determination of structures of adsorbed molecules is indicated.

INTRODUCTION

The method of electron stimulated desorption ion angular distributions (ESDIAD) can provide information regarding surface bonding site symmetry and local bonding configuration /1,2/. The positive ions which desorb from an adsorbed layer during low energy ( $\sim 100$  eV) electron bombardment have been found to desorb in discrete focused beams in directions related to the symmetry of the single crystal substrate. The desorption of ions in discrete beams is apparently related to the formation of localized bonds at the surface.

In order to test experimentally the relationship between ion desorption angle and the bond angle in an adsorbed molecule (or surface complex), we are studying the adsorption of physisorbed and weakly chemisorbed species, i.e., systems whose bonding geometry should only be weakly perturbed by adsorption. The present discussion concerns the adsorption of  $\text{NH}_3$  and  $\text{H}_2\text{O}$  on the close packed (001) surface of hcp Ru. Because of the lone pair electrons on the N and O atoms in these two molecules, it was anticipated that the primary interaction with the Ru surface would be via the N and O atoms; the hydrogen end of the adsorbed molecules should therefore be directed away from the surface. The ESDIAD results for  $\text{H}_2\text{O}$  and  $\text{NH}_3$  adsorbed on  $\text{Ru}(001)$  are in agreement with this model, and a combination of LEED, ESDIAD and thermal desorption studies are used to provide insights into the bonding in these systems. The present brief account is a report of work in progress, and it will be amplified in greater detail elsewhere /3/.

EXPERIMENTAL

The ultrahigh vacuum apparatus used for these studies has been described previously /2,3/. Briefly, a focused electron beam (100 to 300 eV) bombards a  $\text{Ru}(001)$  crystal onto which  $\text{H}_2\text{O}$  or  $\text{NH}_3$  has been adsorbed using a molecular beam doser. The ion beams which desorb from the crystal by electron stimulated desorption (ESD) pass through a hemispherical grid and are accelerated to a microchannel plate (MCP) assembly. The output signal from the MCP assembly is displayed visually on a fluorescent screen and photographed. Mass identification of ESD ions are made using a quadrupole mass spectrometer (QMS). In addition, the QMS may be used as a detector in thermal desorption studies from the adsorbed layers. The cleanliness of the  $\text{Ru}(001)$  crystal was verified using Auger Electron Spectroscopy.

RESULTS

A.  $\text{H}_2\text{O}$  on  $\text{Ru}(001)$

Thermal desorption studies indicate that the dominant mode of  $\text{H}_2\text{O}$  chemisorption on  $\text{Ru}(001)$  at 90 K is as an undissociated molecule; mass 18  $\text{H}_2\text{O}$  is the primary thermal desorption product. ( $\text{H}_2\text{O}$  also adsorbs molecularly on clean and carburized  $\text{Ni}(110)$  /4/ and on  $\text{Si}(111)$  /5/.) Following saturation of the chemisorbed monolayer (which is observed to thermally desorb following first order kinetics), multilayers of  $\text{H}_2\text{O}$  were observed to condense on the surface at 90 K. The multilayers desorb thermally following zero order kinetics (indicative of free sublimation) with an activation energy of 11.5 kcal/mole, in good agreement with the heat of sublimation of ice.



Examination of  $H_2O$  adsorption using ESD indicates that for low coverages ( $\theta \lesssim 0.2$ ),  $H^+$  ions desorb in a hollow conical distribution resulting in an ESDIAD pattern having the appearance of a "halo" of  $H^+$  ions (Figure 1a,b). As the coverage of adsorbed  $H_2O$  increases, the  $H^+$  ion pattern becomes hexagonally symmetric, as schematically illustrated in Fig. 1c. Finally, for  $H_2O$  coverages  $\gtrsim 1$  monolayer, an intense beam of  $H^+$  ions normal to the surface is observed (Fig. 1d). Mass analysis of the ESD ions indicated that for all the patterns of Fig. 1, the dominant ionic species detected was  $H^+$ . As will be discussed below, the ESDIAD data for fractional monolayer coverages of  $H_2O$  are consistent with a model in which  $H_2O$  is bonded to the Ru(001) surface via the O atom, with H atoms directed away from the surface /3/.

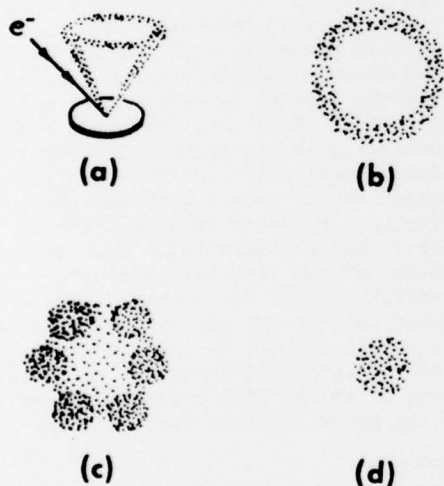


Fig. 1. Schematic ESDIAD patterns for  $H_2O$  and  $NH_3$  on Ru(001) at 90 K

- (a) Formation of hollow cone of  $H^+$  ions from adsorbed  $NH_3$  and  $H_2O$
- (b) "Halo"  $H^+$  pattern characteristic of low coverages
- (c) Hexagonal  $H^+$  pattern characteristic of intermediate coverages (less than 1 monolayer)
- (d) Normal (central spot)  $H^+$  pattern from ice multilayer

## B. $NH_3$ on Ru(001)

Thermal desorption studies of  $NH_3$  on Ru(001) suggest that  $NH_3$  is primarily molecularly adsorbed at 90 K; the dominant thermal desorption product is mass 17  $NH_3$ . Chemisorbed  $NH_3$  thermally desorbs in a sequence of binding states in the temperature range  $\sim 180$  K to  $\sim 340$  K. The presence of multiple overlapping states did not permit unequivocal determination of desorption order. Following saturation of the chemisorbed states, condensed multilayers of  $NH_3$  form on the surface upon further exposure to gaseous  $NH_3$ . The thermal desorption results are in reasonable agreement with the recent data of Danielson et al. /6/ for  $NH_3$  on Ru(001).

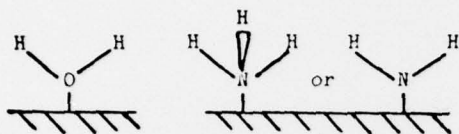
ESD studies of adsorbed  $NH_3$  indicate that the low coverage chemisorbed layer formed at 90 K yields a hollow, conical array of  $H^+$  ions very similar to the ESDIAD pattern observed for low  $H_2O$  coverages (Fig. 1a,b). At higher coverages, a hexagonal pattern similar to that of Fig. 1c is seen. However, the  $H^+$  hexagon from  $H_2O$  has the same orientation as the Ru(001) substrate hexagonal array whereas the  $H^+$  hexagon from  $NH_3$  is rotated  $30^\circ$  (Fig. 2).

Upon heating the  $NH_3$  layer formed at 90 K the "halo" decreases in intensity but does not disappear until  $T \sim 320$  K, where the thermal desorption data indicates that desorption of  $NH_3$  is essentially complete. ESD of condensed  $NH_3$  multilayers results in an intense beam of  $H^+$  emission in the direction normal to the surface as illustrated in Fig. 1d. An adsorption model consistent with these results is presented below.

## DISCUSSION

Molecular orbital calculations and gas phase ultraviolet photoemission spectroscopy (UPS) measurements indicate that  $H_2O$  and  $NH_3$  both possess non-bonding (lone pair) electrons on the O and N atoms, respectively /7/. It is expected that the initial interaction between  $H_2O$  (or  $NH_3$ ) and a transition metal surface should be via the lone pair orbitals located primarily on the oxygen (nitrogen) end of the molecule. Evidence for the molecular adsorption of  $H_2O$  is fairly strong, although infrared studies /8/ of  $NH_3$  adsorbed on highly dispersed Ru supported on  $SiO_2$  indicate the possible formation of  $NH_2$  and  $NH$  groups as well as coordinated  $NH_3$ .

Schematically, models of  $\text{H}_2\text{O}$  and  $\text{NH}_3$  adsorption consistent with the thermal desorption data and the "halo" ESDIAD patterns are given by:



ESD of  $\text{H}_2\text{O}$  and  $\text{NH}_3$  bonded through O and N results in  $\text{H}^+$  emission in non-normal directions. The "halo" is envisioned to occur either because azimuthal orientations of the adsorbed molecules are random and non-coordinated, or because the adsorbed molecules may be freely rotating.

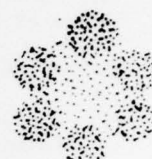
Additional evidence for the adsorbed  $\text{H}_2\text{O}$  structure comes from a measurement of the  $\text{H}^+$  emission angle. The cone angle of the region of maximum intensity of the  $\text{H}^+$  halo from  $\text{H}_2\text{O}$  is estimated to be  $116 \pm 10^\circ$ , in comparison with the  $104.5^\circ$  HOH angle of the free molecule. The fact that the ion desorption angle is greater than  $104.5^\circ$  may be due to several factors, including the image force on the desorbing  $\text{H}^+$  ion and the influence of surface bonding and charge transfer on the HOH angle (e.g., the HOH angle in free  $\text{H}_2\text{O}^+$  is measured to be  $110.6^\circ/9^\circ$ ). Similar measurements are underway for  $\text{NH}_3$ , and (hopefully) will permit us to distinguish between the possible adsorption models.

At higher  $\text{H}_2\text{O}$  coverages ( $\theta > 0.2$  monolayers), lateral interactions between neighboring molecules apparently result in the formation of domains in which the orientations of the  $\text{H}_2\text{O}$  molecules are coordinated with the hexagonal symmetry of the substrate. This is interpreted as the cause of the hexagonal  $\text{H}^+$  ESDIAD pattern illustrated in Fig. 1c. Note that no ordered LEED pattern other than the  $(1 \times 1)$  pattern characteristic of the clean substrate was seen during  $\text{H}_2\text{O}$  adsorption at 90 K, so that if ordered domains having other symmetry exist, they can have only short range order (domain size  $\sim 15 \text{ \AA}/10^\circ$ ). Lateral interactions also result in a similar orientational effect in the  $\text{NH}_3$  layer at coverages slightly less than a monolayer. A major difference between the respective  $\text{H}^+$  hexagons from  $\text{H}_2\text{O}$  and  $\text{NH}_3$  is their orientation with respect to the underlying Ru substrate (Fig. 2). If the N (and O) are bonded to single Ru

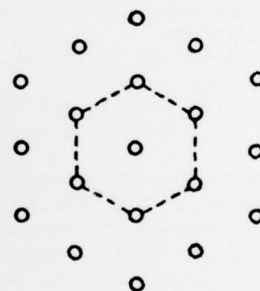
substrate atoms, the azimuthal orientations of the hexagons suggest that the H atoms in  $\text{H}_2\text{O}$  are located in planes joining nearest neighbor substrate atoms, whereas the H atoms in  $\text{NH}_3$  are located in the direction of the three-fold vacant sites.



(a)  $\text{NH}_3$



(b)  $\text{H}_2\text{O}$



(c) Ru(001) Lattice

Fig. 2. Azimuthal orientation of hexagonal  $\text{H}^+$  ESDIAD patterns for  $\text{NH}_3$  and  $\text{H}_2\text{O}$  adsorbed on Ru(001) at 90 K

(a)  $\text{NH}_3$ ;  $0.5 \lesssim \theta < 1$

(b)  $\text{H}_2\text{O}$ ;  $0.2 \lesssim \theta < 1$

(c) Ru(001) substrate

Finally, multilayers of both  $\text{NH}_3$  and  $\text{H}_2\text{O}$  yield  $\text{H}^+$  ions in a direction normal to the surface. This suggests that NH and OH bonds point outward in a normal direction from the thick layers of vitreous  $\text{NH}_3$  and  $\text{H}_2\text{O}$  ices formed upon condensation at 90 K.

#### CONCLUSION

The ESDIAD method is able to provide unique information about structures of adsorbed molecules, even in the absence of long range order. Of particular interest is the apparent ability to detect the conformation of the hydrogen ligands, which is not easily

accomplished using LEED. We await independent verification of the conclusions regarding adsorbed  $H_2O$  and  $NH_3$  using other surface sensitive structural techniques, such as LEED or angular resolved UPS.

#### ACKNOWLEDGEMENT

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